band at 1329 cm^{-1}, and this is consistent with an isocyanate structure.[18] Bis(cyclopentadienyl)titanium(IV) dicyanate also was assigned the isocyanate structure on the basis of the presence of two infrared bands at 1300 and 1370 cm^{-1}.[19] It is not possible to state with confidence whether the thiocyanate and selenocyanate are bound through nitrogen or the group VI atom. Coutts and Wailes[19] have suggested that the titanium compound $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$ is nitrogen bonded because of the absence of an infrared band in the region 650–800 cm^{-1}. The spectrum of the vanadium analog is similar. On the other hand Giddings[20] suggests bonding through sulfur for the titanium compound and classifies the bis(cyclopentadienyl)titanium(IV) moiety as a soft acid because of its ease of reaction with thiols compared to alcohols. With bis(cyclopentadienyl)vanadium(IV), the stability of the cyanate and azide make the isothiocyanate and isoselenocyanate structures plausible. Although much effort has been made to determine the mode of attachment of SCN^- and $SeCN^-$ from vibrational spectra, these questions cannot be settled with any degree of confidence on the basis of infrared data alone, especially when the low-frequency vibrations occur with very low intensity as is the case here.

Acknowledgments.—Financial support to G. D. in the form of Du Pont and NSF summer fellowships is gratefully acknowledged.

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[18] See the discussion by J. S. Thayer and R. West, *Advan. Organometal. Chem.*, **5**, 115 (1967).

[19] R. S. P. Coutts and P. C. Wailes, *Australian J. Chem.*, **19**, 2069 (1966).

[20] S. A. Giddings, *Inorg. Chem.*, **6**, 849 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA 55455

Isolation of Complex Halogeno Anions as the Acetylacetonatobis(cyclopentadienyl)titanium(IV) and -vanadium(IV) Salts. Reactions of $(\pi\text{-}C_5H_5)_2Ti^{IV}$ and $(\pi\text{-}C_5H_5)_2V^{IV}$ with Squarate and Ethyl Acetoacetate Ions[1,2]

BY GERALD DOYLE[3] AND R. STUART TOBIAS

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The complex anions $FeCl_4^-$, $CoCl_4^{2-}$, $ZnCl_3(H_2O)^-$, $SnCl_3^-$, $CdCl_4^{2-}$, and $SnCl_6^{2-}$ have been precipitated from aqueous solutions of the metal chlorides in the presence of excess chloride ion by the cations $(\pi\text{-}C_5H_5)_2Ti(acac)^+$ and $(\pi\text{-}C_5H_5)_2V(acac)^+$. Conductivity measurements indicate that these compounds are all electrolytes in nitrobenzene solution. Reaction of $(\pi\text{-}C_5H_5)_2Ti^{IV}$ with the squarate ion, $C_4O_4^{2-}$, gives a compound where squarate appears to function as a simple bidentate ligand behaving much like tropolonate. Reactions of $(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$ and $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$ with ethyl acteoacetate give complexes of the type $[(\pi\text{-}C_5H_5)_2M(C_6H_9O_3)]ClO_4$, M = Ti and V. In the vanadium compound the ethyl acetoacetate ligand is chelated normally, while the titanium analog appears to involve coordination *via* one keto oxygen and the "ether" oxygen.

Introduction

In previous communications we have described reactions in aqueous solution of $(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$[4] and $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$[5] with bidentate ligands. Very slightly soluble compounds of the type $[(\pi\text{-}C_5H_5)_2ML]ClO_4$ were obtained where M = Ti(IV) or V(IV) and L is the conjugate base of acetylacetone, benzoylacetone, dibenzoylmethane, and tropolone. Analogous salts were obtained when perchlorate was replaced by other large uninegative anions like BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $F_3CSO_3^-$, $Cl_3CSO_3^-$, $(C_6H_5)_4B^-$, I^-, NCS^-, and $NCSe^-$.

It was only possible to coordinate one bidentate ligand to the bis(cyclopentadienyl)titanium(IV) or -vanadium(IV) moiety, and it was suggested that the ease of preparation of these mono-β-diketonate complexes resulted from the very low solvation energy of the complex cation. This suggested that many uninegative complex halogeno anions present in aqueous solution might be isolated as salts of these large cations. This communication describes the isolation of a number of such chloro complexes.

Although there is a very close parallel between the reaction of analogous bis(cyclopentadienyl)titanium(IV) and -vanadium(IV) compounds, the reaction with ethyl acetoacetate is one case where different products are obtained. Structures are suggested for these two compounds.

In an effort to force the coordination of more than two oxygen atoms about the bis(cyclopentadienyl)titanium(IV) moiety, the squarate complex was synthesized. Several compounds of the type $M(C_4O_4)\cdot 2H_2O$ with dipositive transition metal cations have been prepared, and it has been suggested that they have a

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[1] Supported, in part, by the National Science Foundation, Grant GP-5022.

[2] Taken from a thesis submitted by G. D. to the Graduate School of the University of Minnesota for the Ph.D. degree, 1967.

[3] NASA Trainee, 1965–1967.

[4] G. Doyle and R. S. Tobias, *Inorg. Chem.*, **6**, 1111 (1967).

[5] G. Doyle and R. S. Tobias, *ibid.*, **7**, 2479 (1968).

long-chain polymeric structure with bridging squarate groups and octahedral coordination of the metal ion.[6]

Experimental Section

Salts of the 2,4-Pentanedionatobis(cyclopentadienyl)titanium(IV) and -vanadium(IV) Ions with Complex Chloro Anions.—A solution of $[(\pi\text{-}C_5H_5)_2Ti(acac)]^+Cl^-$ or $[(\pi\text{-}C_5H_5)_2V(acac)]^+Cl^-$ was formed by stirring a suspension of $(\pi\text{-}C_5H_5)_2TiCl_2$ or $(\pi\text{-}C_5H_5)_2VCl_2$ in water containing excess acetylacetone for 1 hr and filtering. The filtrate was added to a solution of the metal chloride, and the resulting precipitate was collected on a frit, washed, and dried.

Reactions with Ethyl Acetoacetate. (Ethyl acetoacetato)bis(cyclopentadienyl)titanium(IV) Perchlorate.—A mixture of 50 ml of dry ethyl acetoacetate, $(\pi\text{-}C_5H_5)_2TiCl_2$ (1.25 g, 0.005 mol), and anhydrous $AgClO_4$ (2.07 g, 0.01 mol) was stirred for several minutes until precipitation was complete. The solution was filtered to remove AgCl, and the solvent was removed on a rotary evaporator at 50° (0.5 mm). When most of the solvent had been removed, a deep red oil remained, and this was washed several times with moist ether. The insoluble solid material which was obtained was ground under ether giving a red violet powder which was collected on a frit and dried under vacuum. *Anal.* Calcd for $C_{16}H_{19}ClO_7Ti$: C, 47.3; H, 4.71; Cl, 8.72. Found: C, 46.8; H, 4.30; Cl, 8.72.[7] Infrared bands were observed at 3016 m*, 2981 w, 2930, vw, 1717 s, 1657 sh, 1641 s, 1576 s, 1566 s, 1516 s, 1469 w, 1439 m*, 1396 m, 1381 w, 1367 w, 1331 w, 1321 w, 1291 s, 1278 s, 1213 m, 1183 m, 1091 vw**, 1058 m, 1013 s*, 972 m, 921 w, 887 m, 837 s*, 798 m, 778 m, 757 vw, 706 w, 684 m, 647 w, 623 s*, 581 w, 575 w, 505 m, 470 m, 433 w, 374 m (*, $(\pi\text{-}C_5H_5)_2Ti^{IV}$ vibrations; **, ClO_4^- vibrations). All of the perchlorates will detonate and should be handled with care.

(Ethyl acetoacetato)bis(cyclopentadienyl)vanadium(IV) Perchlorate.—To 50 ml of dry ethyl acetoacetate was added $(\pi\text{-}C_5H_5)_2VCl_2$ (1.25 g, 0.005 mol) and anhydrous $AgClO_4$ (2.1 g, 0.01 mol). The mixture was stirred for 30 min, the AgCl was removed by filtration, and the solvent was removed by evaporation on a rotary evaporator at *ca.* 45° (1 mm). When approximately one-fourth of the solvent had been removed, a gray precipitate began to form. This product was collected on a frit, washed with ether, and dried under vacuum. The compound appeared to be an adduct of $HClO_4$ and $[(\pi\text{-}C_5H_5)_2V(C_6H_9O_3)]ClO_4$. *Anal.* Calcd for $C_{16}H_{19}ClO_7V \cdot 1.5HClO_4$: C, 34.3; H, 3.68; Cl, 15.8. Found: C, 34.1; H, 4.57; Cl, 15.2.

When this compound was washed with moist ether to remove the excess $HClO_4$, the color turned gradually to olive green. The same green compound can be obtained from $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$ in ethyl acetoacetate if slightly moist solvents are employed. No solid formed until almost all of the solvent had been removed by evaporation. The green residue was suspended in ether, collected on a frit, and vacuum dried. The compound was so explosive that combustion analyses could not be carried out. Infrared bands were observed at 3109 s*, 2981 m, 2936 vw, 2870, 1584, 1563 vs, 1515 vs, 1475 w, 1444*, 1431 m, 1409 w, 1365 m, 1294 vs, 1176 s, 1091 vs**, 1065 sh, 1016 m*, 990 w, 974 m, 840 s*, 784 s, 744 w, 623 s**, 492 m, 434 w, 405 vw, 344 w (*, $(\pi\text{-}C_5H_5)_2V^{IV}$ vibrations; **, ClO_4^- vibrations).

(Ethyl acetoacetato)bis(cyclopentadienyl)vanadium(IV) Trifluoromethanesulfonate, $[(\pi\text{-}C_5H_5)_2V(C_6H_9O_3)]F_3CSO_3$.—To 50 ml of ethyl acetoacetate was added with stirring $(\pi\text{-}C_5H_5)_2VCl_2$ (1.5 g, 0.006 mol). Small portions of AgF_3CSO_3 were added until AgCl no longer precipitated. The mixture was filtered, and the solvent was removed from the filtrate on a rotary evaporator at 45° (0.5 mm). The insoluble solid, green product was stirred with several portions of ether and then THF, collected on a frit, and dried under vacuum; yield 1.4 g, 51%. *Anal.* Calcd for $C_{17}H_{19}F_3O_6SV$: C, 44.4; H, 4.17; F, 12.4; S, 6.98. Found: C, 44.5; H, 3.86; F, 11.9; S, 6.14. Infrared bands were observed at 3108 s*, 2981 m, 2935 vw 2870 vw, 1587 vs, 1555 s, 1514 vs, 1469 w, 1448 m*, 1431 m, 1405 w, 1368 m, 1294 vs, 1260 vs**, 1220 s**, 1173 s, 1152 s**, 1126 w**, 1058 m, 1028 s**, 1015 sh, 988 w, 972 m, 840 s*, 800 vw, 776 s**, 750 m, 737 w, 635 s**, 609 w**, 571 m**, 517 m**, 489 m, 430 w, 405 vw (*, $(\pi\text{-}C_6H_5)_2V^{IV}$ vibrations; **, $F_3CSO_3^-$ vibrations[8]).

1,2-Dihydroxycyclobutenedionatobis(cyclopentadienyl)titanium(IV), $(\pi\text{-}C_5H_5)_2Ti(C_4O_4)$.—Squaric acid, 1,2-dihydroxycyclobutenedione, was prepared from 1,2-dichlorotetrafluorocyclobutene by the method of West, *et al.*[9] This was converted to the dipotassium salt by adding the equivalent amount of KOH to the acid. To a solution of $(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$ (0.005 mol) in 50 ml of water was added a slight excess of $K_2C_4O_4$. The reddish orange precipitate which formed immediately was collected on a frit, washed several times with water, ethanol, and ether, and dried under vacuum, mp *ca.* 220° dec. *Anal.* Calcd for $C_{14}H_{10}O_4Ti$: C, 58.0; H, 3.77. Found: C, 56.8; H, 3.87. Infrared bands were observed at 3090 m*, 1786 m, 1691 s, 1532 vs, b, 1435 s, b, 1399 vs, 1355 m, 1063 m, 1012 m*, 874 w, 826 s*, 815 s, 738 m, 676 m, 431 w, 401 m, 383 m, 348 w, 327 w (*, $(\pi\text{-}C_5H_5)_2Ti^{IV}$ vibrations).

Infrared Spectra.—The infrared spectra were recorded on a Perkin-Elmer 521 spectrometer using the split-mull technique and both NaCl and CsI windows. Calibration was effected with polystyrene film.

Conductivity Measurements.—Conductivities were measured with the apparatus and procedures described previously.[5]

Results

Chloride analyses and conductivity data for the salts containing the complex chloro anions are listed in Table I.

TABLE I

CHLORIDE ANALYSES AND MOLAR CONDUCTIVITIES OF SALTS CONTAINING COMPLEX CHLORO ANIONS

Compound[a]	% chloride Calcd	% chloride Found	Molar conductivity[b] ohm^{-1} cm^2	Molar conductivity[b] Concn, *M*
$[(\pi\text{-}Cp)_2Ti(acac)][FeCl_4]$	29.9	30.9	31.4	0.00060
$[(\pi\text{-}Cp)_2Ti(acac)][SnCl_3]$	21.2	21.6	27.2	0.00053
$[(\pi\text{-}Cp)_2Ti(acac)][HgCl_3]$	18.2	18.1	29.7	0.00040
$[(\pi\text{-}Cp)_2Ti(acac)][ZnCl_3(H_2O)]$	22.8	22.7	26.2	0.00166
$[(\pi\text{-}Cp)_2Ti(acac)]_2[CdCl_4]$	17.5	17.4	56.5	0.00030
$[(\pi\text{-}Cp)_2Ti(acac)]_2[SnCl_6]$	24.0	23.6	*c*	. . .
$[(\pi\text{-}Cp)_2V(acac)][FeCl_4]$	29.5	28.8	29.7	0.00136
$[(\pi\text{-}Cp)_2V(acac)][SnCl_3]$	21.0	21.0	27.0	0.00119
$[(\pi\text{-}Cp)_2V(acac)][HgCl_3]$	18.1	17.7	*c*	. . .
$[(\pi\text{-}Cp)_2V(acac)]_2[CoCl_4]$	18.6	19.2	54.6	0.00020
$[(\pi\text{-}Cp)_2V(acac)]_2[CdCl_4]$	17.4	17.8	51.5	0.00043
$[(\pi\text{-}Cp)_2V(acac)]_2[SnCl_6]$	23.8	24.0	*c*	. . .

[a] π-Cp = $\pi\text{-}C_5H_5$. [b] Nitrobenzene solution, 25°; values in the range 22–34 ohm^{-1} cm^2 are typical for 1:1 electrolytes while values of 38–53 ohm^{-1} cm^2 are characteristic of 2:1 electrolytes: C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 375 (1956). [c] Conductivity measurements could not be made on these salts because of their extremely low solubility.

Vibrational frequencies for some of the complex chloro anions are listed in Table II, and the spectra below 600 cm^{-1} for several are illustrated in Figure 1.

The infrared spectra of $[(\pi\text{-}C_5H_5)_2Ti(C_6H_9O_3)]ClO_4$ and the vanadium(IV) analog are illustrated in Figure 2. The equivalent conductivity for the titanium

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(6) R. West and N. Y. Niu, *J. Am. Chem. Soc.*, **85**, 2589 (1963).

(7) Microanalyses by Clark Microanalytical Laboratory, Urbana, Ill.

(8) Assignments of the $F_3CSO_3^-$ vibrations were made on the basis of unpublished Raman and infrared studies by M. G. Miles, G. Doyle, and R. S. Tobias.

(9) R. West, H. Y. Hiu, and M. Ito, *J. Am. Chem. Soc.*, **85**, 2584 (1963).

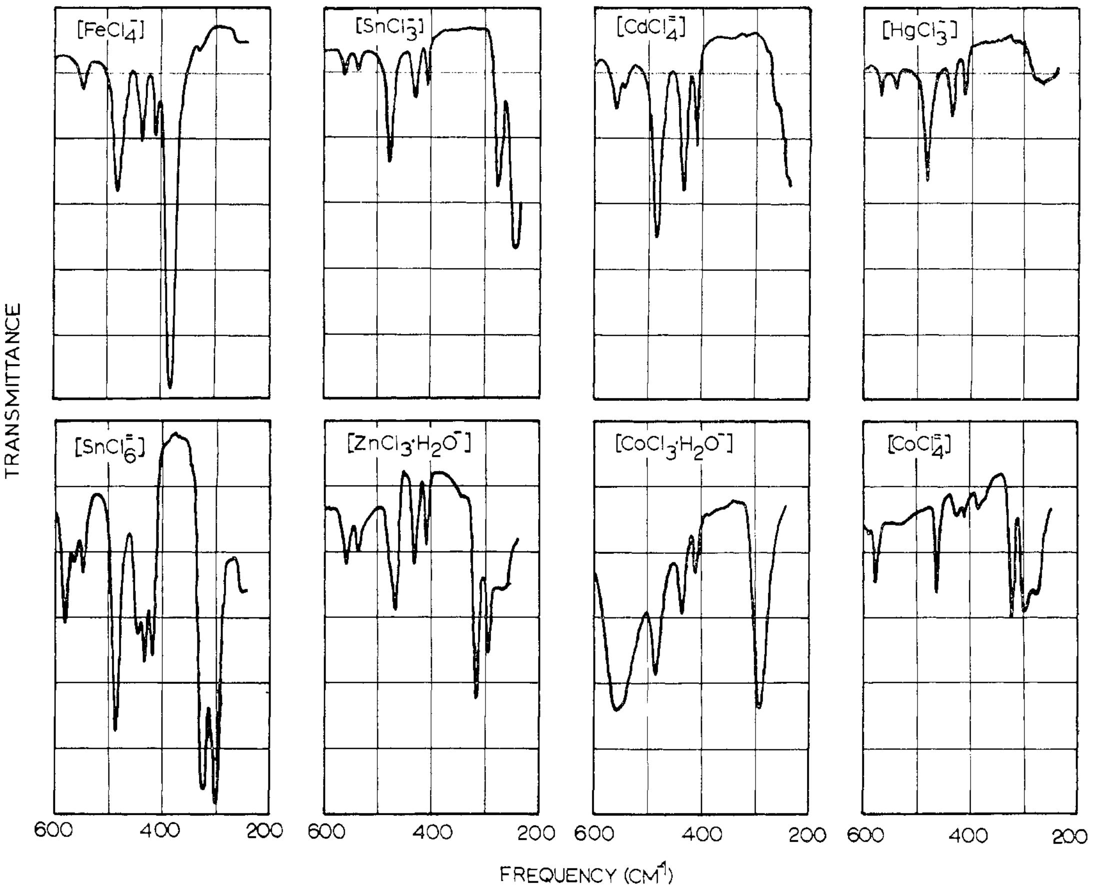


Figure 1.—Vibrational spectra for several bis(cyclopentadienyl)titanium(IV) and -vanadium(IV) salts containing complex chloro anions.

Table II

Anion Vibrations for Some Salts Containing Complex Chloro anions

Compound	ν(M–Cl), cm^{-1} Obsd	Lit.
$[(\pi\text{-Cp})_2\text{Ti(acac)}][\text{HgCl}_3]$	276 vb, m	282, 287 (Raman, melt[a])
$[(\pi\text{-Cp})_2\text{Ti(acac)}][\text{SnCl}_6]$	303 s, 314 s	313 (ir, mull[b]) 311 (Raman, aq, ir inactive[c])
$[(\pi\text{-Cp})_2\text{Ti(acac)}][\text{FeCl}_4]$	329 vw, 380 vs	330 (ir inactive), 385 (Raman, aq[d])
$[(\pi\text{-Cp})_2\text{Ti(acac)}][\text{SnCl}_3]$	240 s, 290 s	256, 297 (Raman, soln[e])
$[(\pi\text{-Cp})_2\text{Ti(acac)}][\text{ZnCl}_3(\text{OH}_2)]$	295 s, 320 s	286 (Raman, aq[f])
$[(\pi\text{-Cp})_2\text{V(acac)}][\text{CoCl}_4]$	302 m	297 (ir, mull[g])

[a] G. J. Janz and D. W. James, *J. Chem. Phys.*, **38**, 905 (1963). [b] J. Haraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **20**, 819 (1964). [c] L. A. Woodward and L. E. Anderson, *J. Chem. Soc.*, 1248 (1957). [d] L. A. Woodward and M. J. Taylor, *ibid.*, 4473 (1960). [e] L. A. Woodward and M. J. Taylor, *ibid.*, 407 (1962). [f] D. F. C. Morris, E. L. Short, and D. N. Waters, *J. Inorg. Nucl. Chem.*, **25**, 975 (1963). [g] A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

compound was 27.4 ohm^{-1} cm^2 (0.00065 M) and that for the vanadium compound was 37.2 ohm^{-1} cm^2 (0.00058 M). With the trifluoromethanesulfonate anion, the vanadium chelate had a molar conductivity of 32 ohm^{-1} cm^2 (0.00068 M). All values were determined at 25° with nitrobenzene solutions.

Discussion

Many uninegative chloro complexes can be isolated from aqueous solution as the bis(cyclopentadienyl)titanium(IV) and -vanadium(IV) salts. With the exception of bands assigned to the anions, the infrared spectra are all the same as for the perchlorate and trifluoromethanesulfonate salts.[4,5] Consequently, it is extremely unlikely that any of these salts involve halide bridging to the titanium or vanadium atoms. The titanium complex cation should be especially useful for isolating anionic complexes, since it is diamagnetic and does not absorb in much of the visible region of the spectrum.

In most cases, a uninegative complex anion is precipitated from the metal chloride solutions, and the conductivity data indicate that these compounds all behave as 1:1 electrolytes in nitrobenzene solution. Only in the cases of Cd(II), Co(II), and Sn(IV) are dinegative anions precipitated, perhaps indicating that low concentrations of the uninegative complex ions are present in the solutions which have high concentrations of chloride ion. In all cases, the metal–chlorine stretching frequencies observed in the infrared spectra are consistent with the presence of the complex chloro anions. With Zn^{2+}, an aquotrichlorozincate(II) anion is precipitated, and the coordinated water can be identified by its intense infrared absorption. Isolation of this $ZnCl_3(H_2O)^-$ anion is of some interest, since it has been

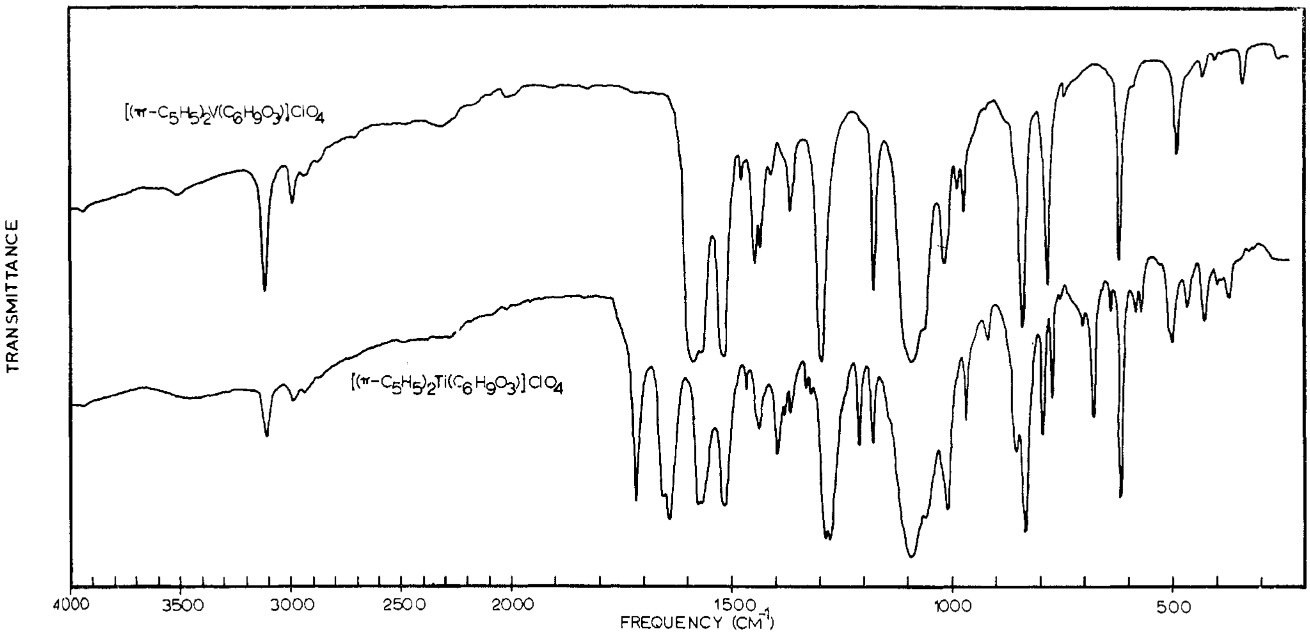
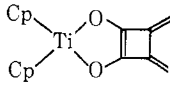


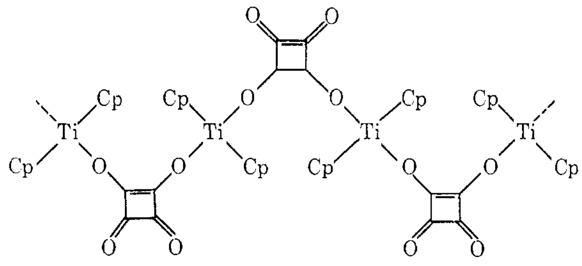
Figure 2.—Infrared spectra of the ethyl acetoacetate chelates $[(\pi\text{-}C_5H_5)_2Ti(C_4H_9O_3)][ClO_4]$ and $[(\pi\text{-}C_5H_5)_2V(C_4H_9O_3)][ClO_4]$.

suggested on the basis of Raman spectra of aqueous $ZnCl_2$ solutions containing excess chloride ion that the tetrachlorozincate ion is octahedral, *i.e.*, that it is diaquotetrachlorozincate(II).[10] More recent studies of these solutions by Quicksall and Spiro[11] have indicated that this is incorrect and that $ZnCl_4^{2-}$ is tetrahedral. Irish, *et al.*, found no evidence for the trichloro complex from their Raman spectra, while Morris, *et al.*,[12] did. Gilbert[13] in interpreting his Raman spectra of these solutions assumed the trichloro complex to be absent. Although structures can change from the solution to the solid state and the precipitation of a complex from solution does not necessarily mean that it is the predominant species in solution, the isolation of $[(\pi\text{-}C_5H_5)_2Ti(acac)][ZnCl_3(H_2O)]$ does indicate that the aquotrichlorozincate(II) is a rather stable ion.

The squarate complex has the empirical formula $(\pi\text{-}C_5H_5)_2TiC_4O_4$. The infrared spectrum is not in agreement with the polymeric structure with bridging squarate ions as is apparently formed in $NiC_4O_4 \cdot 2H_2O$, $MnC_4O_4 \cdot 2H_2O$, and $CuC_4O_4 \cdot 2H_2O$. The vibrational spectrum would appear to be much too complex for such symmetrical coordination of the squarate ion. In the divalent transition metal hydrate complexes, there are only four infrared bands which can be attributed to the squarate ligand indicating that the effective symmetry is very high. For $(\pi\text{-}C_5H_5)_2TiC_4O_4$, there are 16 infrared bands between 300 and 1800 cm⁻¹ which are assigned to the squarate ligand. Assignments of the vibrations localized primarily in the bis(cyclopentadienyl)titanium(IV) moiety were made on the basis of the earlier studies.[4] The divalent transition metal compounds also give no carbonyl bands above 1600 cm⁻¹ which is good evidence that all four oxygen atoms are coordinated to the metal ion. With $(\pi\text{-}C_5H_5)_2TiC_4O_4$, there is a medium-intensity band at 1786 and a strong band at 1691 cm⁻¹ indicating uncoordinated oxygens. In this compound, the squarate ion appears to be behaving as a bidentate ligand. A monomeric structure (I) is possible. The extremely low solubility of the compound ($<10^{-4}$ *M* in $C_6H_5NO_2$, much less in less polar solvents) suggests that the squarate may be bridging (II). Because of the very low solubility, molecular weights could not be obtained to distinguish between these.



I



II

Since the acid dissociation constant for ethyl acetoacetate is comparable to that of the β-diketones, it was thought that complexes of bis(cyclopentadienyl)titanium(IV) and -vanadium(IV) with this β-keto ester similar to those of the β-diketones could be synthesized. When reactions similar to those used for the preparation of the latter complexes were carried out, *i.e.*, the reaction of ethyl acetoacetate with aqueous solutions of $(\pi\text{-}C_5H_5)_2Ti(ClO_4)_2$ and $(\pi\text{-}C_5H_5)_2V(ClO_4)_2$, no complexes could be isolated. Using ethyl acetoacetate as the solvent, $[(\pi\text{-}C_5H_5)_2Ti(C_6H_9O_3)]ClO_4$ is formed. With slightly moist solvents, the vanadium

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(10) D. E. Irish, B. McCarroll, and T. F. Young, *J. Chem. Phys.*, **38**, 3436 (1963).

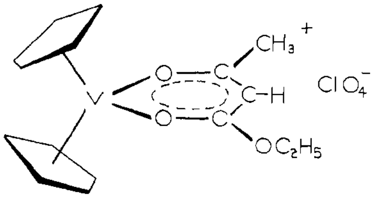
(11) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **5**, 2232 (1966).

(12) See footnote *f* of Table II.

(13) B. Gilbert, *Bull. Soc. Chim. Belges*, **76**, 493 (1967).

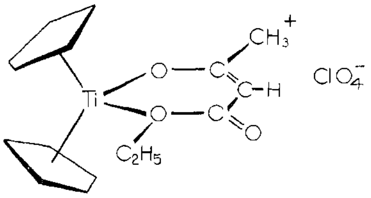
analog was also prepared. Because of the extremely explosive nature of the latter compound, good analyses could not be obtained. However, $[(\pi\text{-}C_5H_5)_2V(C_6H_9O_3)]F_3CSO_3$ was prepared under the same conditions, and the infrared spectra of the perchlorate and trifluoromethanesulfonate are identical except for the anion vibrations. Under anhydrous conditions, a complex perchlorate with the approximate composition $[(\pi\text{-}C_5H_5)_2V(C_6H_9O_3)]ClO_4 \cdot 1.5HClO_4$ was obtained, and this could be freed of perchloric acid by washing with moist ether. The compounds are both very insoluble in inert solvents such as benzene and chloroform, and dissolution in acetonitrile, dimethylformamide, or dimethyl sulfoxide is accompanied by reaction and displacement of the β-keto ester ligand. Reaction of either compound with concentrated hydrochloric acid yielded the bis(cyclopentadienyl)metal dichloride. This, together with the analyses, shows that the formulation as bis(cyclopentadienyl) complexes is correct.

A comparison of the infrared spectra of the titanium and vanadium ethyl acetoacetate complexes shows that they must have fundamentally different structures. Although the characteristic frequencies of the cyclopentadienyl groups and the perchlorate ion can be seen in the spectra of both salts, the ethyl acetoacetate ligand vibrations are distinctly different. In the case of the vanadium compound, the lack of any free carbonyl absorption above 1600 cm^{-1} suggests that the ligand is chelated through the two keto oxygens in $[(\pi\text{-}C_5H_5)_2V(C_6H_9O_3)]ClO_4$. The close similarity of the infrared spectrum to that of the acetylacetonate analog indicates that the compound has structure III. This ionic structure is supported by the fact that the conductivity in dilute nitrobenzene solutions is typical for a 1:1 electrolyte.



III

In the case of the titanium compound $[(\pi\text{-}C_5H_5)_2Ti(C_6H_9O_3)]ClO_4$, the presence of intense infrared bands at 1717, 1657, and 1641 cm^{-1} is good evidence for a free carbonyl group in the molecule (the carbonyl absorptions of free ethyl acetoacetate (92.5% keto form) occur at approximately 1725 and 1745 cm^{-1}). The conductivity data indicate that this compound is also a 1:1 electrolyte. Unfortunately, the very low solubility made it impossible to obtain a pmr spectrum. The infrared spectrum, together with the molar conductivity and analytical data, suggests a bidentate chelate structure with coordination through one keto oxygen and the "ether" type oxygen atom (IV). This structure, together with the observation that the coordinated ligand of the vanadium compound can be protonated in perchloric acid solution, suggests that the keto and ether oxygens are of comparable donor strengths. Several titanium(IV) chelates with β-keto esters such as $Cl_2Ti(C_6H_9O_3)_2$[14] and $Ti(OCH_3)_2(C_6H_9O_3)_2$[15] have been prepared and are very similar to the analogous β-diketonate complexes. They have been assumed to have the normal chelate structure. The steric requirements of an ethyl acetoacetate ligand would not be much greater than the acetylacetonate group; moreover, if steric effects were important they should be more pronounced with the smaller vanadium atom.



IV

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[14] D. M. Puri and R. C. Mehrota, *J. Less-Common Metals*, **3**, 247 (1961).

[15] D. M. Puri and R. C. Mehrota, *ibid.*, **3**, 247 (1961).